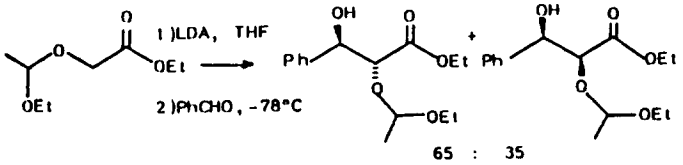
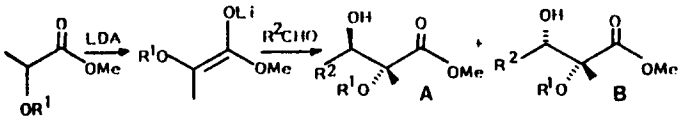
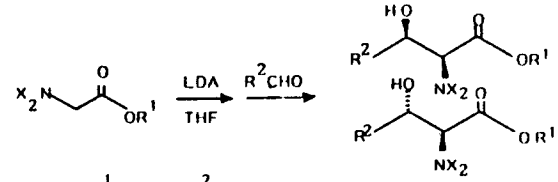


A.M.Touzin, TET.LETT., 1975, 1477.

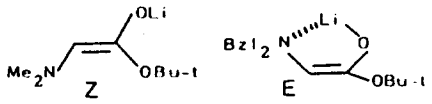


A/B = 70:30 - > 97:3

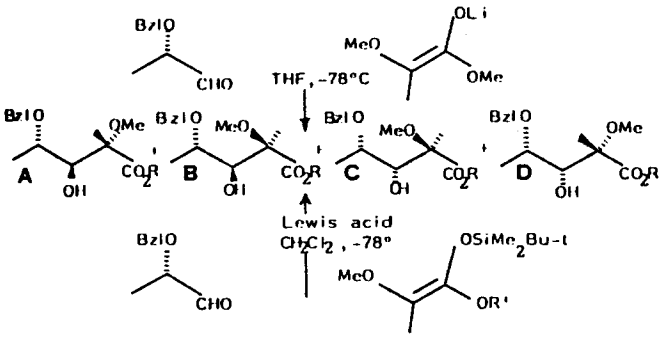
C.H.Heathcock, J.P.Hagen, E.T.Jarvi, M.C.Pirrung, S.D.Young, J.Am. Chem.Soc., 103, 1981, 4972.



X	R^1	R^2	Syn/Anti	T(°C)	t(min)
Me	t-Bu	Me	50/50	-78	5
Me	t-Bu	Ph	75/25	78	5
Me_3Si	Me_3Si	Me	0/100	-78 (60'),	
Me_3Si	Me_3Si	Ph	0/100	then 0°(30')	
Bzl	t-Bu	Me	55/45	-60	5
Bzl	t-Bu	Ph	18/82	-60	5
Bzl	t-Bu	n-Hex	46/54	-60	5
Bzl	t-Bu	c-Hex	16/84	-60	5
Bzl	t-Bu	t-Bu	20/80	-60	5

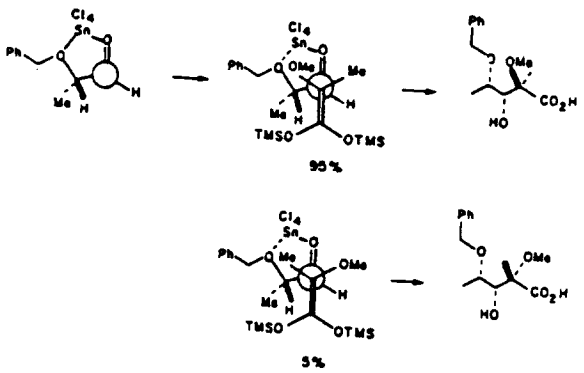


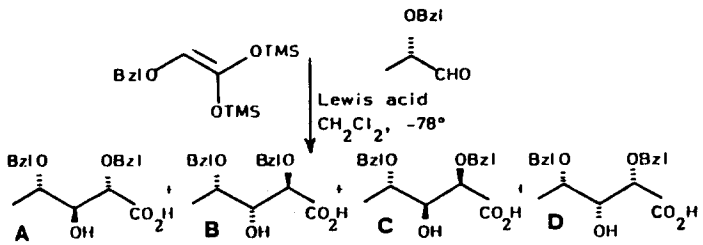
A.M.Touzin, TETR.LETT., 1975, 1477; A.Shanzer, J.O.C., 44, 1979, 3967; G.Guanti, L.Banfi, E.Narisano, C.Scolastico, TETR.LETT., 1984, 4693.



Conditions	R	R'	A	B	C	D
Li-enolate	Me	-	70	23	7	0
$BF_3.OEt_2$	Me	Me	-	-	67	33
$SnCl_4$	H	$SiMe_2Bu^t$	-	-	95	5

C.H.Heathcock, S.H.Montgomery, TET.LETT., 1001, (1985)

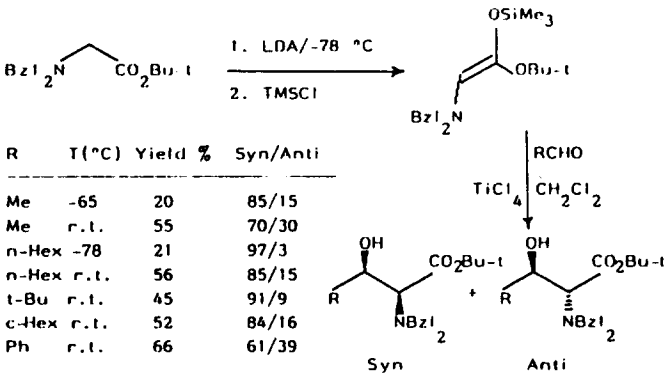




C-2,C-3 Simple Diastereoselection (A+B),(C+D)
C-3,C-4 Diastereofacial Selectivity(A+C),(B+D)

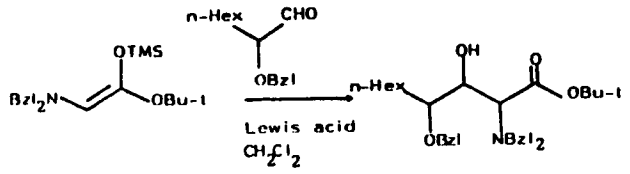
Lewis Acid	Yield %	C-2,C-3	C-3,C-4
$BF_3.OEt_2$	34	62:38	40:60
$SnCl_4$	43	68:32	28:72
$TiCl_4$	58	62:38	34:66
$MgBr_2$	28	19:81	1:99
$ZnCl_2$	26	68:32	1:99

K.Takai, C.H.Heathcock, J.Org.Chem., 50, 3247, (1985).



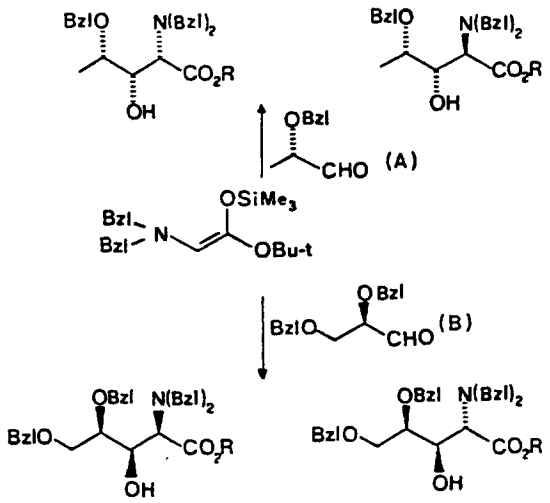
R	T(°C)	Yield %	Syn/Anti
Me	-65	20	85/15
Me	r.t.	55	70/30
n-Hex	-78	21	97/3
n-Hex	r.t.	56	85/15
t-Bu	r.t.	45	91/9
c-Hex	r.t.	52	84/16
Ph	r.t.	66	61/39

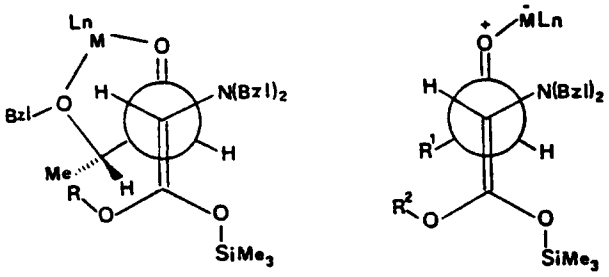
G.Guanti, L.Banfi, E.Narisano, C.Scolastico, Tetr.Lett., 1985, 3517.



Lewis Acid	T(°C)	Yield%	Diastereomeric ratio (TLC spectrodensitometry)
$SnCl_4$	-78	53	25:59:0:16
$TiCl_4$	-78	55	27:50:7:16

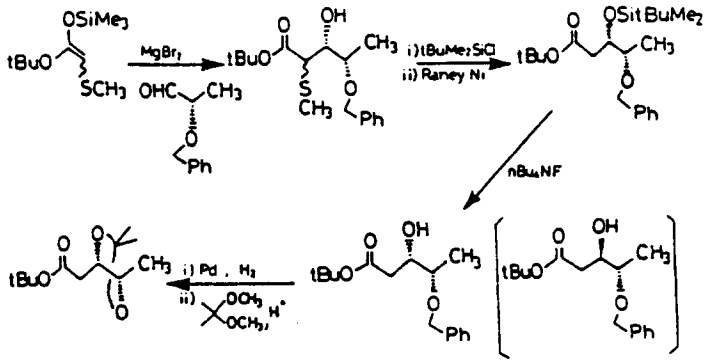
G.Guanti, L.Banfi, E.Narisano, C.Scolastico, TET.LETT., 1985, 3517.





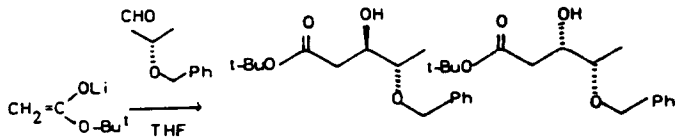
Z ⟶ 2,3-Syn 3,4-Syn

Z ⟶ Syn



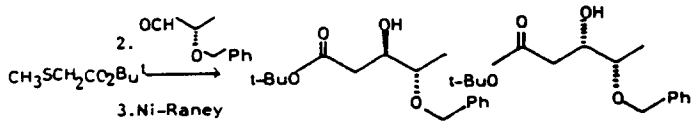
Syn/Anti 99:1

J-i Huenishi, H.Tomozane, M.Yamato, TET.LETT., 1985, 3467.



3 : 2

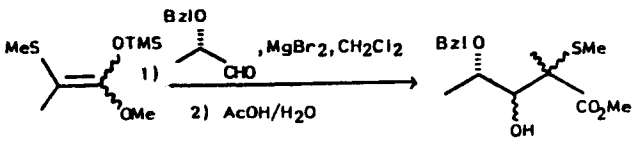
Cram cyclic Cram

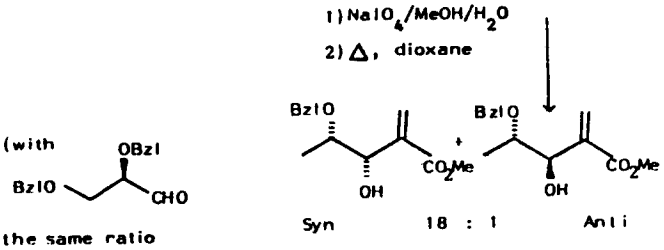


88 : 12

Cram cyclic Cram

J-i Uenishi, H.Tomozane, M.Yamato, J.C.S.Chem.Comm., 1985, 717.

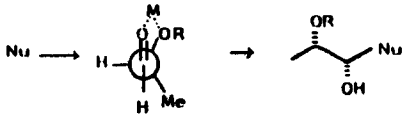




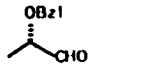
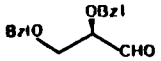
Syn 18 : 1 Anti

(with the same ratio Syn/Anti 18:1 was obtained)

A.Bernardi, S.Cardani, C.Gennari, G.Poli, C.Scolastico, TET.LETT. 6509 (1985)

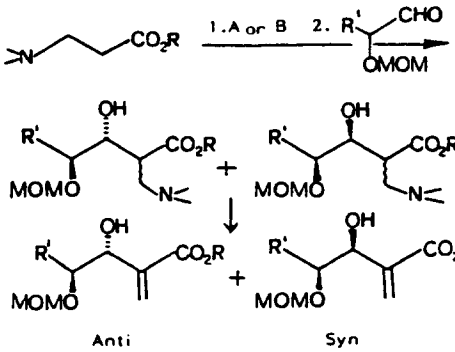


ADDITION OF SILYL KETENE ACETAL OF METHYL α-METHYLTHIO PROPIONATE TO ALKOXY ALDEHYDES.

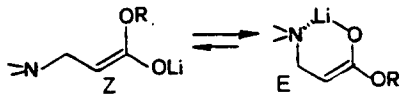
Aldehyde	Lewis Acid	Condensation Conditions	Syn/Anti
	$SnCl_4$	-78°C/1h	1.1:1
	$ZnCl_2$	-40°C/3h	2:1
	$MgBr_2$	-40°C/3h	11:1
	$MgBr_2$	-78°C/8h	18:1
	$MgBr_2$	-78°C→ 0°C	18:1
	$SnCl_4$	-78°C/4h	1:3

(1mol.equiv. of the Lewis acid to a solution of the aldehyde in CH_2Cl_2, followed by addition of silylketene acetal)

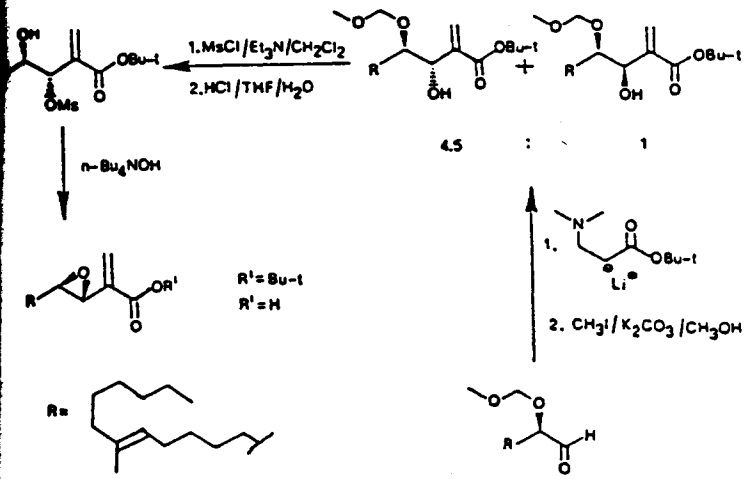
A.Bernardi,S.Cardani,C.Gennari,G.Poli,C.Scolastico, TET.LETT., 1985, 6509.

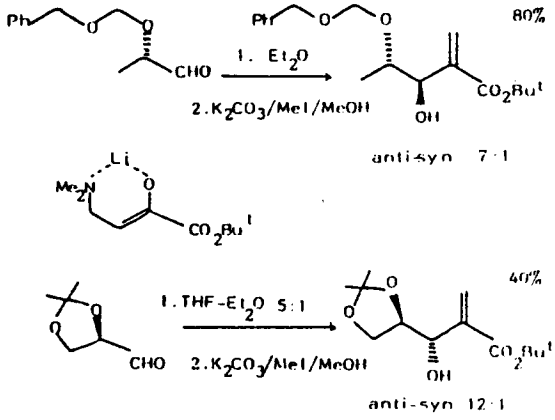


A: LDA/THF/-78°C up to Anti/Syn 4:1
B: LDA/Et_2O/ 0°→-78° " 24:1

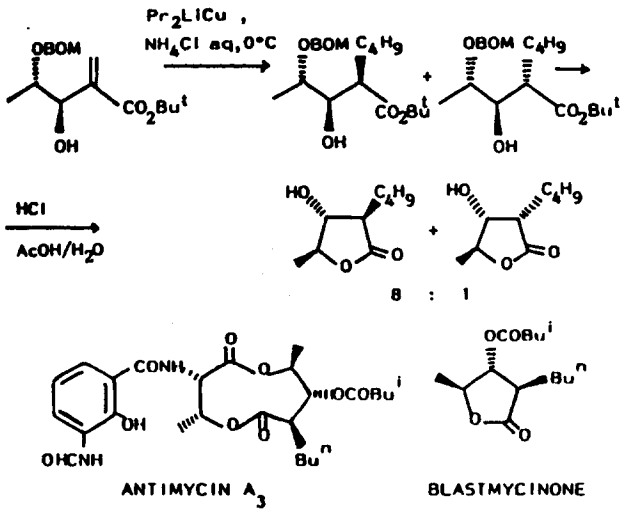


L.Banfi,A.Bernardi,L.Colombo,C.Gennari, C.Scolastico, J.O.C.,49,3784(1984)

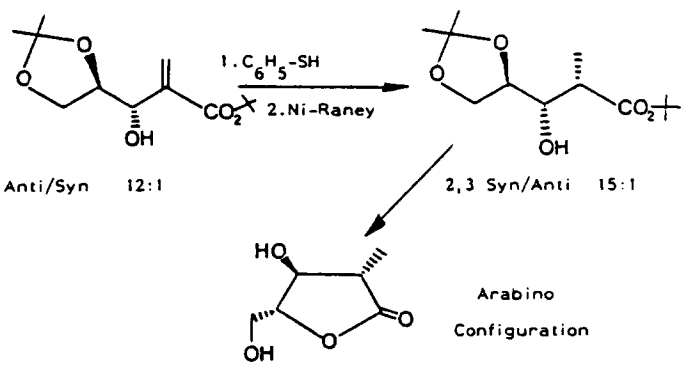




A.Bernardi,M.G.Beretta,L.Colombo,C.Gennari,G.Poli, C.Scolastico, J.Org.Chem., 1985, 4442.

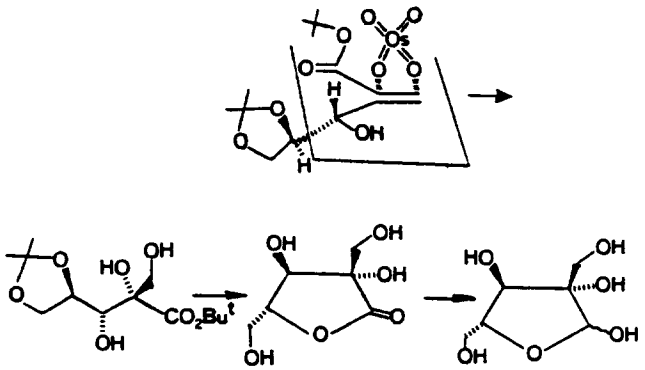


A.Bernardi,M.G.Beretta,L.Colombo,C.Gennari,G.Poli, C.Scolastico, J.Org.Chem., 1985, 4442.

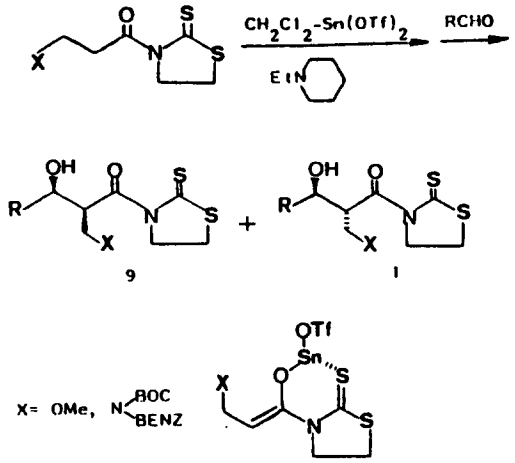


A.Bernardi, M.G.Beretta, L.Colombo, C.Gennari, G.Poli, C.Scolastico, J.O.C., 50, 4442(1985).

OSMYLATION OF THE DOUBLE BOND

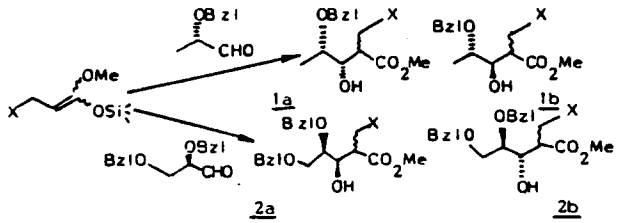


A.Bernardi, M.G.Beretta, L.Colombo, C.Gennari, G.Poli, C.Scolastico, J.O.C., 50, 4442(1985)



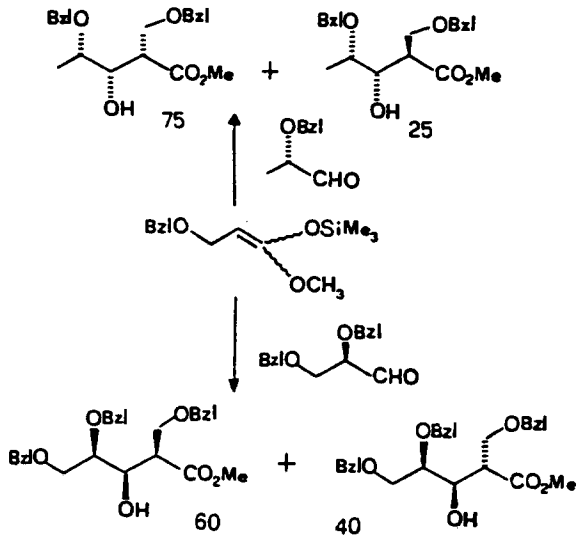
N.Wasawa, H.Huang, T.Mukayama, CHEM.LETT., 1985, 1045.

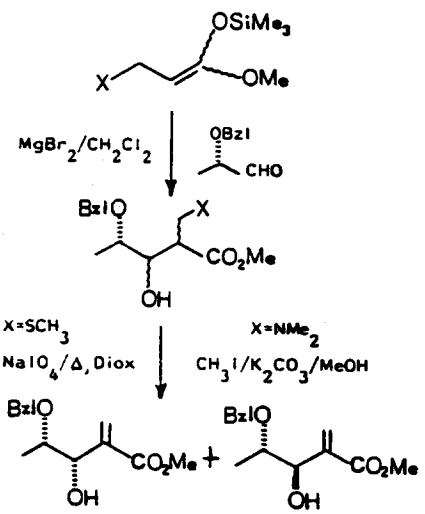
DIASTEREOFACIAL SELECTIVITY (C-3,C-4)

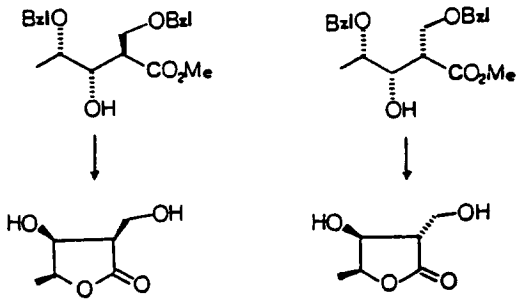


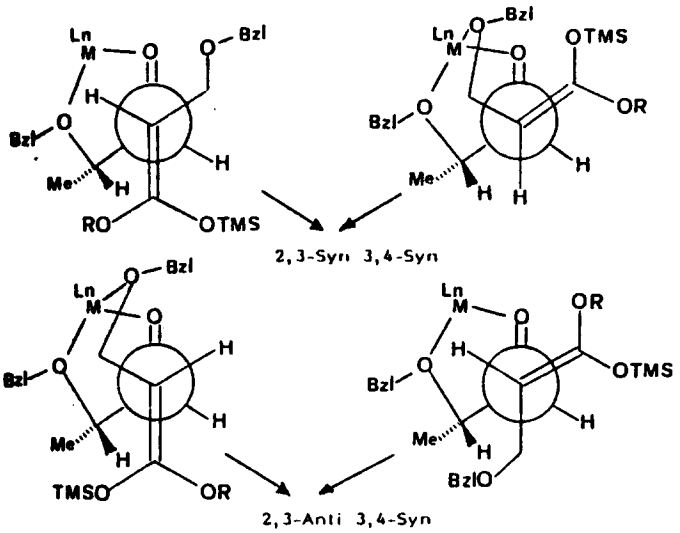
X	L.A.	1a/1b	Yield%	2a/2b	Yield%
-SMe	$TiCl_4$	dec.	—	—	—
	$SnCl_4$	dec.	—	—	—
	$MgBr_2$	>24:1	80	>55:1	75
-OBzl	$TiCl_4$	dec.	—	—	—
	$SnCl_4$	dec.	—	—	—
	$MgBr_2$	>50:1	80	>50:1	81
$-NMe_2$	$TiCl_4$	16:1	15	—	—
	$SnCl_4$	2.8:1	15	—	—
	$MgBr_2$	>44:1	20	>53:1	18

C-2,C-3 SIMPLE DIASTEREOSELECTION





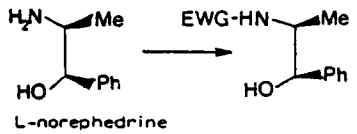




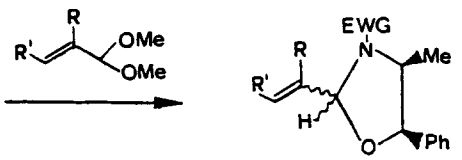
CHARACTERISTICS OF CHIRALLY MASKED α,β-UNSATURATED ALDEHYDES.

1. FAIR DEGREE OF π-FACE DIFFERENTIATION
2. EASY SEPARATION OF THE DESIRED OPTICALLY PURE DIASTEREOMER
3. SIMPLE REMOVAL AND RECYCLING OF THE CHIRAL DIRECTING GROUP
4. COMMERCIAL AVAILABILITY OF BOTH THE ENANTIOMERIC FORMS OF THE CHIRAL AUXILIARY

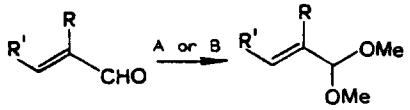
SYNTHESIS OF 2-ALKENYLOXAZOLIDINES



L-norephedrine



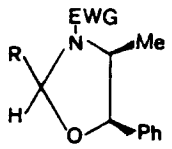
EWG: $PhCH_2OCO$, t-BuCO, $p\text{-}C_7H_7SO_2$, PhCO, MeOCO.



A. $HC(OMe)_3/NH_4NO_3/MeOH$

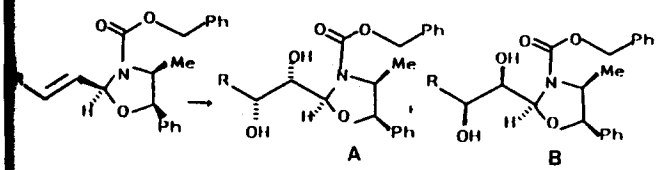
B. $(MeO)_4Si/MeOH/85\%\ H_3PO_4$

Cis/Trans RATIO OF 2-ALKENYLOXAZOLIDINES



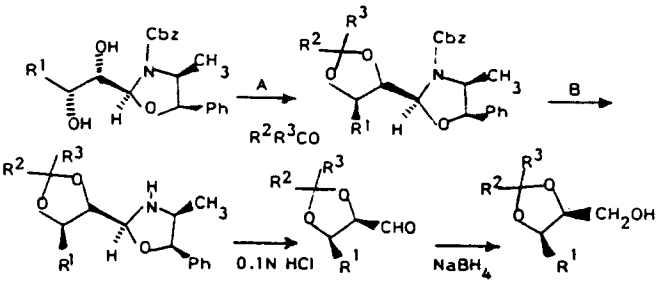
R	EWG	Cis/Trans
(E) $PhCH_2OCH_2CH$=CH	$PhCH_2OCO$	5:1
(E) MeCH=CH	"	7:1
(E) MeO_2CCH=CH	"	100:0
(E) MeCH=CMe	MeOCO	8:1
Me_2CHC=CH_2	"	60:1
$Me((CH_2)_2C$=CH_2	"	150:1
(E) MeO_2CCH=CH	"	200:1
(E) MeCH=CH	$p\text{-}C_7H_7SO_2$	100:0
(E) MeO_2CCH=CH	"	50:1
(E) MeCH=CH	t-BuCO	18:1
CH_2=CH	"	100:0

DIHYDROXYLATION OF 2-ALKENYL OXAZOLIDINES.



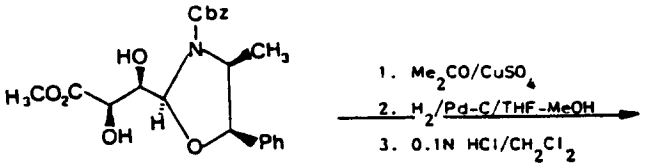
R	Reactive	t (h)	T°C	Solvent	Yield%	A/B
CH_3	OsO_4 cat. Me_3N→O	25	25	Me_2CO/H_2O 8/1	76	3.4/1
$BzlOCH_2$	"	25	25		88	3.5/1
CO_2Me	$KMnO_4$ $n\text{-}C_{16}H_{33}NMe\ Br$	20	-40	CH_2Cl_2	60	1/4
CO_2Me	OsO_4 cat. Me_3N O	20	25	Me_2CO/H_2O 8/1	95	1/2.7

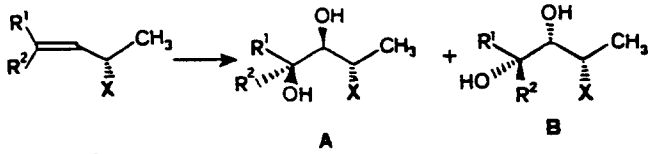
L.Colombo, C.Gennari, G.Poli, C.Scolastico, S.De Munari, TETR.LETT., 1985, 5459.



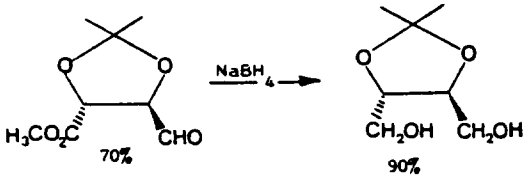
R^1	R^2, R^3	A Yield%	B Yield%	C Yield%	D Yield%
Me	$-(CH_2)_5$	85	99	95	52
$PhCH_2OCH_2$	Me, Me	90	95	95	55

L.Colombo, C.Gennari, G.Poli, C.Scolastico, S.De Munari, TETR.LETT., 1985, 5459.





J.K.CHA, W.J.CHRIST. J.KISHI.
TETRAHEDRON, 40, 2247(1984)



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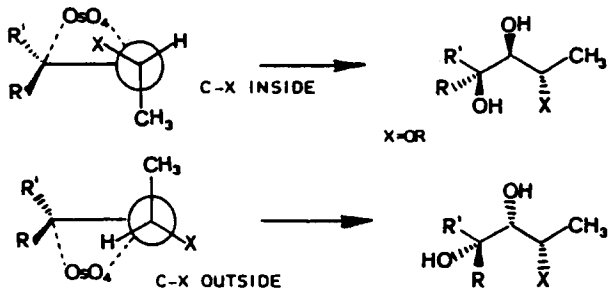

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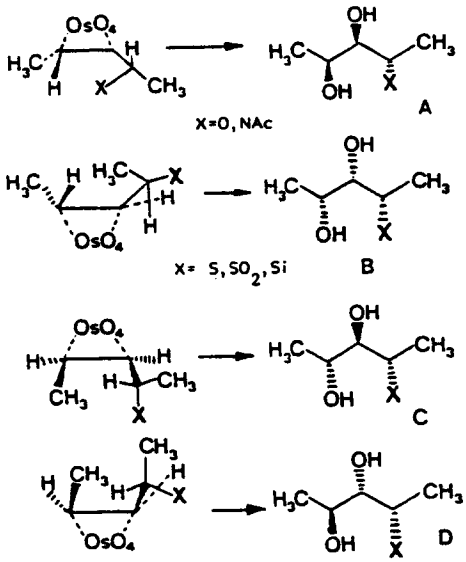

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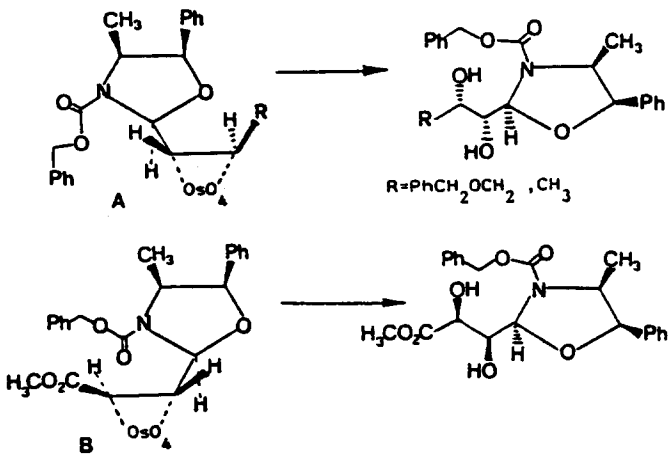
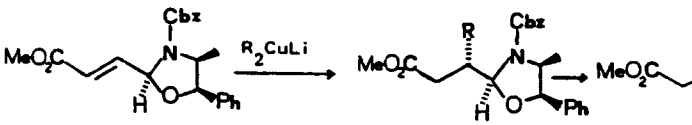
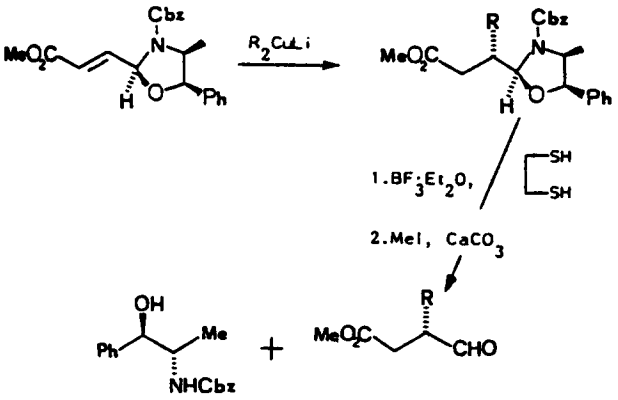
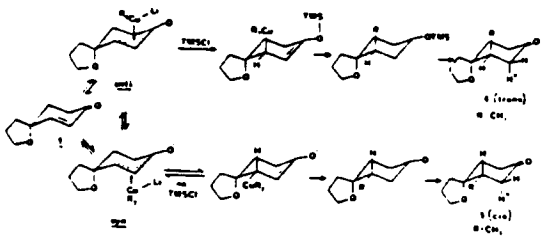




CUPRATE	TEMP.	CONFIG.	R	YIELD%	e.e.%
Me_2CuLi	-25°	S	Me	68	93
Me_2CuLi/TMSCl	-78°	S	Me	75	93
Bu_2CuLi	-25°	S	Bu	70	91
Et_2CuLi	-25°	S	Et	70	90
$Vinyl_2CuLi$	-50° → -25°	R	CH_2=CH	75	--

Diastereomeric ratio always >95:5





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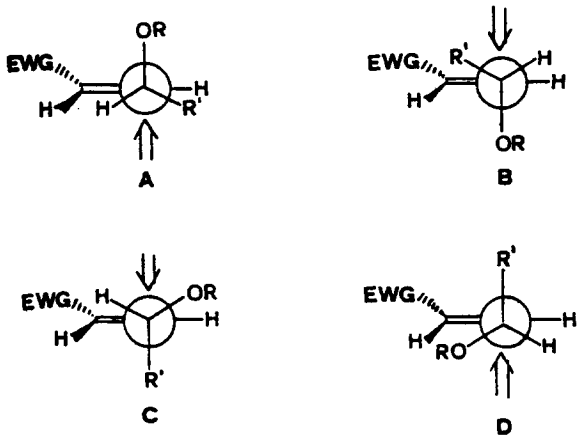

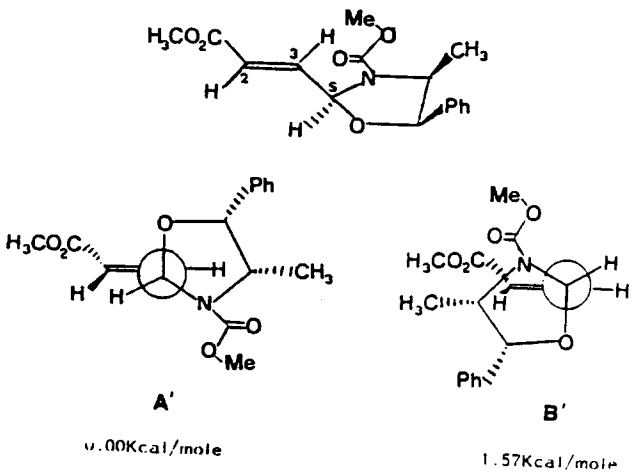

R

YIELD

85

85

80

84

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